Materials Letters 62 (2008) 3751–3753

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Metallization of electrospun polyacrylonitrile fibers by gold

Shizhen Zhao, Bin Guo, Gaoyi Han *, Yanni Tian

Institute of Molecular Science, Key Laboratory of Chemical Biology and Molecular Engineering of Education Ministry, Shanxi University, Taiyuan 030006, PR China

ARTICLE INFO

Article history:
Received 1 January 2008
Accepted 14 April 2008
Available online 5 May 2008

Keywords:
Polyacrylonitrile
Gold
Electrospinning
Porous carbon fiber

ABSTRACT

Sub-micrometer fibers of polyacrylonitrile were prepared by using electrospinning technique, and thin continuous gold films were coated on the polyacrylonitrile fibers surface through self-catalyzed reduction of chloroauric acid in solution. The conductivities of the metallized fibrous mats were relatively high and increased with the increase of deposited gold amount. When the metallized fibrous mats were thermally treated at higher temperature, the morphology of the gold films on fibers surface changed, and the morphology changes depended on not only the temperature but also the amount of gold deposited on the fibers surface. Porous carbon fibers were obtained when the thermal treated gold-coated fibers were treated with dilute aqua regia.

1. Introduction

Gold nanostructures and assembled films have attracted a great deal of attention because of their applications in catalysis, electronic devices and photonic sensors [1–4]. Recently, they have been used as plasmon resonance or surface-enhanced Raman (SER) spectroscopy substrates, electrodes, catalyst, and patterns in microscale or nanoscale structures [5–7]. The assembled gold films can be conveniently fabricated on different substrates such as glass or other oxide surfaces, silicon and polymers [8–10].

On the other hand, electrospinning technique has attracted more attention because it is a simple and convenient method for generating organic, inorganic and hybrid fibers with diameters ranging from tens of nanometers to several micrometers [11–19]. The collected electrospun fibers have been used as template for fabricating micro-tube structures of organic and inorganic materials [16]. However, there are few literatures on the metallization of the electrospun organic fibers [17–19].

In this paper, the continuous thin gold films are deposited on the electrospun polyacrylonitrile (PAN) fibers to form the metallized three-dimensional fibrous material with potential application in electrodes or SER substrates. After the mats were thermally treated at different temperatures, the morphology and the conductivity have also been investigated.

2. Experimental procedure

PAN and sodium borohydride were purchased from Aldrich Company. The gold salt was synthesized by using the method of previous literature [18], and other chemicals were reagent grade and used directly.

The gold salt/PAN hybrid fibers were prepared by electrospinning the mixture of PAN (90 mg), tetrabutylammonium bromide (10 mg) and gold salt (10 mg) in 1.0 ml dimethylformamide. The electrospinning potential was +13.7 kV, and the fibers were collected on the filter paper placed upon the grounded aluminum foil below the nozzle tip 12 cm. In order to make the mats more uniform, the collector electrode was often shifted during the process of electrospinning, and the mats selected for metallized were cut from the central part of the mats.

The procedure of preparing the gold-coated PAN fibers was similar to that of previous literature [18]. The mixture of 0.1 mg/ml chloroauric acid and 0.02 mg/ml $NH_2OH{\cdot}HCl$ was used as electroless plating solution. The samples prepared from 200, 400 and 600 ml plating solution were defined as S1, S2 and S3, respectively.

The oxidative stabilization process was carried out by using a conventional muffle furnace at 290 °C for 2 h in air. Thermal treatment of the air-stabilized fibrous mats was performed at 600 and 900 °C, under a high-purity argon atmosphere (99.999%) for 1.5 h, respectively. After thermal treatment at 900 °C, the dilute aqua regia (1.0 mol/L HNO_3 + 3.0 mol/L HCl) was used to treat the gold-coated fibers and carbon fibers prepared from pure PAN fibers.

UV–visible spectra were carried out on Hewlett Packard 8453E single beam diode array recording spectrophotometer. XRD patterns were recorded by using a Bruker D8 Advance X-ray diffractometer from 10° to 80° (2θ) at the speed of 0.02°/s. Scanning electron micrographs were taken out on a microscope (LEO438VP, England) operated at an accelerating voltage of 15 kV, and transmission electron micrographs were carried out on a microscope (H-600-2, Hitachi). The direct current conductivity was measured by conventional four-

* Corresponding author. Tel.: +86 351 7010699; fax: +86 351 7016358.
E-mail address: han_gaoyis@sxu.edu.cn (G. Han).

0167-577X/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2008.04.049

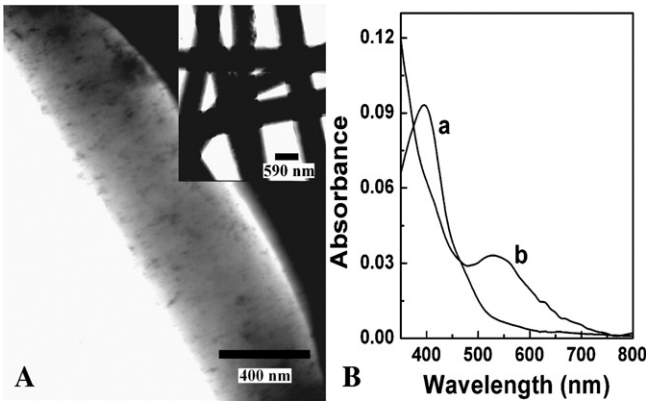

Fig. 1. (A) The TEM images of GNPs/PAN nanofibers and (B) the absorption spectra of the gold salt/PAN nanofibers (a) and GNPs/PAN nanofibers (b).

probe method. The thickness of the mats used for calculating the conductivity was measured as an average one from more than seven points.

3. Results and discussion

The typical TEM image of gold nanoparticles (GNPs)/PAN fibers is shown in Fig. 1A. It can be seen that the diameters of the hybrid fibers range from ~600 nm to ~1000 nm, and the diameters of the GNPs are about 10~15 nm, and there is some aggregation between the GNPs. The gold salt has an absorption peak at about 394 nm (Fig. 1B-a), while the absorption peak of GNPs dispersed in PAN is located at about 528 nm (Fig. 1B-b). According to literature [9], the optical spectrum of spherical gold particles with an average size of 3.4 nm or higher is located at around 520 nm. When the GNPs are aggregated, the absorption peak shifts to longer wavelength. The absorption peak located at 528 nm indicates that there is slight aggregation between the GNPs. This result is consistent with that of TEM.

Fig. 2A shows the SEM micrographs of S1 as prepared, it can be seen that the gold particles have grown from 10~ 15 nm to about 100 nm, and they begin to form a continuous gold layer on most of the fibers surface. When the mats are treated with more plating solution (400 ml), more surfaces of the fibers in S2 are coated with more than one layer of gold particles (Fig. 2B). As 600 ml plating solution is used (S3), the compact continuous gold films with few defects have formed on the fibers surface, and the gold particles grow up to 100~ 200 nm (Fig. 2C). The conductivity of the gold-coated fibrous mats is about 9.19×10^2 (S1), 4.59×10^3 (S2) and 1.01×10^4 S/cm (S3). The gold-coated fibrous mats such as S2 and S3 show a typical golden-yellow reflecting surface.

Table 1
The conductivities of the metallized fibrous mats and carbon fibrous mats

Samples	Conductivity (S/cm)			
	As prepared	After oxidative stabilization	After annealed at 600 °C	After annealed at 900 °C
S1	9.19×10^2	9.70×10^2	7.95×10^2	4.76
S2	4.59×10^3	7.40×10^3	3.21×10^4	18.5
S3	1.01×10^4	1.03×10^4	4.76×10^4	108.1
Carbon fibrous mat	9.31			
Porous carbon fibrous mat	7.21			

After oxidative stabilization, the diameters of gold-coated fibers and the structure of gold films do not show apparent changes, except that some gold particles are coalesced (SFig. 1). The conductivities of the samples increase slightly (Table 1). After the air-stabilized fibrous mats are annealed at 600 °C, the conductivities of S2 and S3 increase while the conductivity of S1 decreases slightly (Table 1). Furthermore, there are obvious structural changes observed for gold films coated on the fibers surfaces. For S1, the thin gold films become incontinuous, and some parts of the fibers are encircled by gold films while some parts of fibers are bare (Fig. 2D). This is possibly due to the fact that the gold films deposited on the surface of S1 are not enough compact to form continuous gold films which can cover the whole surface of the carbon fibers at 600 °C. Besides, there are stronger cohesions among the gold particles than that between gold particles and carbon substrate, so the GNPs coalesce together and leave some naked carbon domains. The diameters of the carbon fibers are estimated to be 500~600 nm from the bare parts of the fibers. For S2, there are more gold particles deposited on the fibers' surface, and the gold particles coalesce together to form larger particles, at the same time the diameter of fibers decreases, which leads to the formation of continuous gold film with cracks (Fig. 2E). For S3, there are more GNPs than S1 and S2, the gold films can keep its structure at 600 °C although some large holes have formed on the gold films because of the coalescence of the gold particles (Fig. 2F). In the previous result, the gold fibers with smooth surface are formed when the gold-coated PMMA fibers are thermally treated at 450 °C [18], but the smooth gold films are not formed when the gold-coated PAN fibers are thermally treated at 600 °C because of the formation of carbon fibers during the thermal treatment.

When the samples are annealed at 900 °C, the conductivities of the metallized fibrous mats decrease dramatically (Table 1). Fig. 3A shows the typical TEM images of S3, which have been annealed at 900 °C. From this figure we can find that the

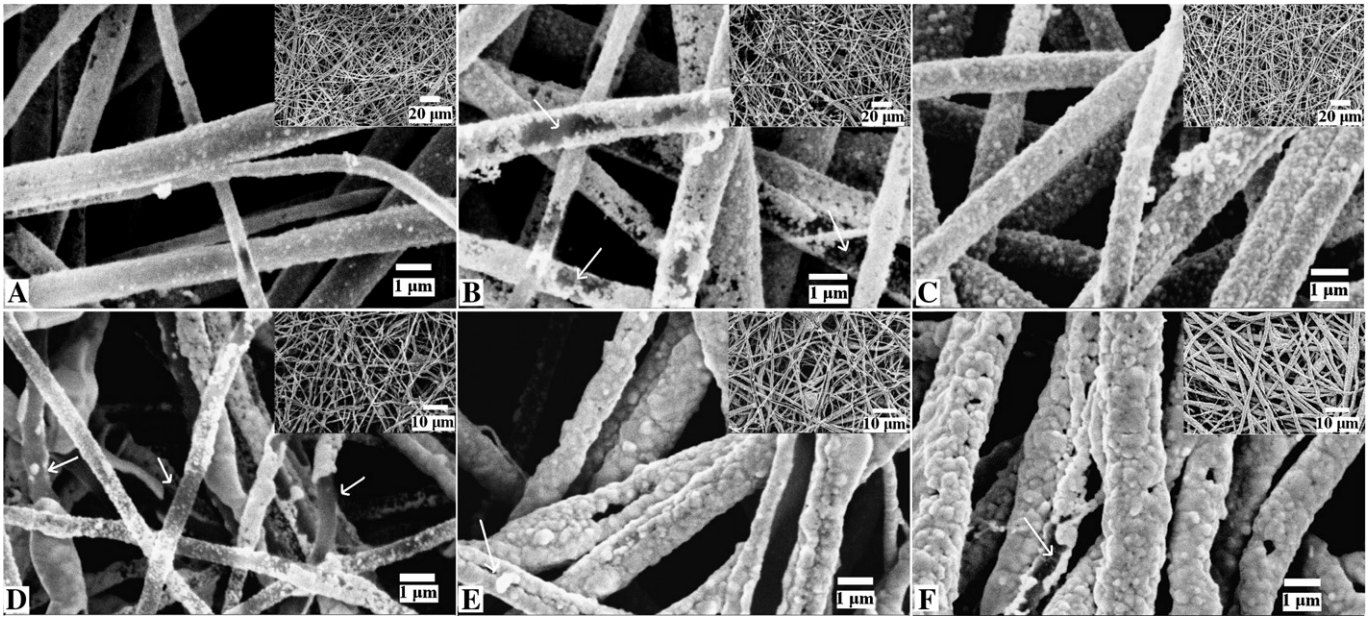

Fig. 2. The SEM images of the gold-coated fibers (A) S1, (B) S2 (the place marked by arrow shows a layer of gold particles below the surface layer), (C) S3, and D), E) and F) after thermally treated S1, S2 and S3 at 600 °C, respectively (the places marked by arrows are the uncovered carbon fibers (D), crack (E) and large hole (F)).

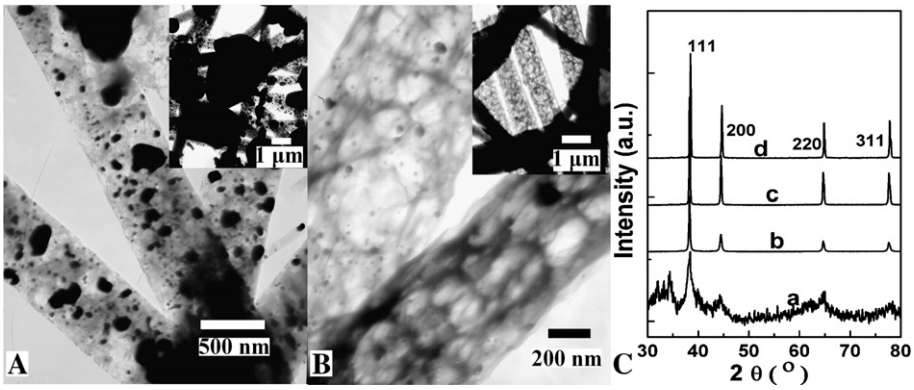

Fig. 3. The TEM images of S3 A) after thermally treated at 900 °C; B) after the gold was dissolved by aqua regia; C) The XRD patterns of (a) GNPs/PAN hybrid fibrous mats, (b) S3 as prepared, (c) and (d) after thermally treated S3 at 600 and 900 °C, respectively.

continuous gold films have been destructed, and gold particles with the size of hundreds nanometers to micrometers are formed and dispersed separately on the surface of the fibers, which leads to remarkable decrease of the conductivities of the mats. When the gold is dissolved by dilute aqua regia, the micro pores ranging from tens to hundreds nanometers are observed in the residual carbonaceous fibers (Fig. 3B). The XRD patterns of the samples (Fig. 3C) show four diffraction peaks, corresponding to the (111), (200), (220) and (311) planes of a face-centered cubic lattice of gold (PDF 4-784). The intensity of (111) plane is much higher than that of other planes (Fig. 3C-b), demonstrating that the (111) plane is the predominant orientation [20]. After the samples are annealed at higher temperature, the ratio value between the intensities of (200) and (111) diffraction peaks becomes close to that of bulk gold (Fig. 3C-c and d), revealing that the (111) plane predominant orientation of the gold coating disappears after thermal treatment.

4. Conclusion

The continuous gold films have been coated on the surface of elecrospun PAN ultrafine fibers by using solution deposition method. The conductivities of the metallized fibrous mats are relatively higher. These metallized fibrous mats may be used as porous electrode for catalysis or SER substrate.

Acknowledgement

Financial support from National Natural Science Foundation of China (20604014), TYAL and Natural Science Foundation of Shaxi Province (2007021008), and Foundation for Young Teachers of Shanxi University.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.matlet.2008.04.049.

References

[1] Sun YG, Xia YN. Adv Mater 2002;14:833–7.
[2] Guzman J, Gates BC. J Am Chem Soc 2004;126:2672–3.
[3] Hutchings GJ. Catal Today 2005;100:55–61.
[4] Ma S, Yu S, Gu Z. Angew Chem Int Ed 2006;45:200–3.
[5] Jin YD, Kang XF, Song YH, Zhang BL, Cheng GJ, Dong SJ. Anal Chem 2001;73:2843–9.
[6] Ren B, Picardi G, Pettinger B, Schuster R, Ertl G. Angew Chem Int Ed 2005;44:139–42.
[7] Wang H, Levin CS, Halas NJ. J Am Chem Soc 2005;127:14992–3.
[8] Supriya L, Claus RO. Langmuir 2004;20:8870–6.
[9] Brown KR, Natan MJ. Langmuir 1998;14:726–8.
[10] Goss CA, Charych DH, Majda M. Anal Chem 1991;63:85–8.
[11] Han GY, Shi GQ. J Appl Polym Sci 2007;103:1490–4.
[12] Frenot A, Chronakis IS. Curr Opin Colloid Inteface Sci 2003;8:64–75.
[13] Li D, Wang YL, Xia YN. Nano Lett 2003;3:1167–71.
[14] Melaiye A, Sun ZH, Hindi K, Milsted A, Ely D, Reneker DH, Tessier CA, Youngs WJ. J Am Chem Soc 2005;127:2285–91.
[15] Li D, Xia YN. Adv Mater 2004;16:1151–70.
[16] Caruso RA, Schattka JH, Greiner A. Adv Mater 2001;13:1577–9.
[17] Bognitzki M, Becker M, Graeser M, Massa W, Wendorff JH, Schaper A, Weber D, Beyer A, Goelzhaeuser A. Adv Mater 2006;18:2384–6.
[18] Han GY, Guo B, Zhang LW, Yang BS. Adv Mater 2006;18:1709–12.
[19] Ochanda F, Jones WE. Langmuir 2007;23:795–801.
[20] Hou ZZ, Abbott NL, Stroeve P. Langmuir 1998;14:3287–97.